

Extract from "Einführung in die Laboratoriumstechnik" (Introduction to laboratory techniques)

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The solution is first of all allowed to cool a little since these substances spontaneously nullify any delays in boiling and violent, explosive boiling may occur. A lot of air escapes from activated charcoal which causes effervescence.

After this the solution is boiled briefly again and then filtered while hot (in connection with this see A.2.1.). The vessel is sealed and then left standing to cool. To augment precipitation the vessel is either placed in a refrigerator or cooled with ice or freezing mixtures.

The tendency to form *supersaturated solutions* is very high in organic substances. Supersaturation can frequently be overcome by introducing "*seed crystals*" of the same or an isomorphous substance. Rubbing the walls of the vessel with a glass rod also creates nuclei of crystallization on whose presence crystallization depends.

The *rate of crystallization* is often very low and, accordingly, crystallization of a chilled solution often takes hours to go to completion. Occasionally, crystalline precipitates still form after weeks or months have elapsed. For that reason mother liquors should not be discarded prematurely.

2.2.3 Crystallization from the melt

Organic substances not only form supersaturated solutions but also readily give rise to supercooled melts. Thus, primarily substances with a low melting point often separate out from solution as oils even below their melting point¹⁾. In this case the solution must be diluted a little more and be cooled down very slowly (e.g. by allowing it to cool down in a previously heated water bath). Crystallization is aided by scraping with a glass rod, rubbing and leaving a drop of the substance on a roughened glass surface or scratching a sample with a highly volatile solvent on a watch glass.

Even after solvents have been distilled off solid organic substances are left behind in the form of an oil, frequently below their melting point. Sometimes they can be made to crystallize only with great difficulty. Nucleation and crystal growth are dependent on temperature in various ways. According to Tamman's rule the maximum for nucleation is approximately 100 °C below the melting point and the maximum crystallization rate is 20 to 50 °C below the melting point (see Fig. A.44).

1) When dissolving by heating the temperature should never be allowed to rise above the melting point but rather should be kept to a maximum of 10 °C below the melting point.

[Figure]

Fig. A.44
Nucleation rate (-----),
Viscosity (_____) and
Crystallization rate (-----)
as a function of temperature

In order to reach the optimum temperature for crystallization the substance is kept for a few hours at approximately 100 °C below the supposed melting point in order to promote nucleation and then the temperature is raised by approximately 50 °.

Homogeneous impurities frequently inhibit nucleation and crystallization. Since in particular entrained and dissolved ground glass joint grease can delay crystallization, ground glass joints should be greased only sparingly, or not at all in the case of special and difficult purification operations.

If crystallization cannot be initiated, purification must be carried out again by a different method (precision distillation, chromatography, partitioning). If there are clues to the nature of the impurities it is possible that rinsing the oil again with special reagents may yield the desired result. Thus, for example, acids can be removed by soda solution, amines by acids and aldehydes by sodium hydrogensulfite.

2.3 Distillation and rectification

Distillation is the most important separation and purification method for liquid substances. In the simplest case of distillation a liquid is brought to the boil by supplying heat and the vapor produced is condensed in a condenser to form the distillate. Since this involves only one phase, that is to say the vapor, it is also known as *direct distillation*. If, on the other hand, a portion of the condensed vapor (the so-called *reflux*) runs counter to the rising vapor and is constantly fed back to the distillation flask we are dealing with *countercurrent distillation*. Countercurrent distillation or *rectification* is carried out in distillation columns.

2.3.1 Dependence of boiling point on pressure

The vapor pressure of a liquid rises steeply with temperature. When it is equal to the external pressure the liquid boils. The temperature dependence of vapor pressure is given by the Clausius-Clapeyron equation:

$$\frac{d \ln p}{dT} = \frac{\Delta_v H}{RT^2} \quad [\text{A.45}]$$

where p is the vapor pressure, $\Delta_v H$ the molar latent heat of evaporation and R the gas constant.

After integration the following equation is obtained:

$$\ln p = \frac{\Delta_v H}{RT} + C \quad [\text{A.46}]$$

(here $\Delta_v H$ is assumed to be independent of the temperature).

Accordingly, when the logarithm of the vapor pressure is plotted against the reciprocal of the absolute temperature a straight line (approximately) is obtained. Such a diagram is shown in Figure A.47 (in the supplement). The gradient of the straight line is determined by the molar latent heat of evaporation and among chemically similar substances having similar boiling points it does not vary very much. Accordingly, from the diagram the boiling points of any organic compounds at any pressures can be approximately determined.

The following rule of thumb may serve as a rough estimate: a reduction of the external pressure by half reduces the boiling point by approximately 15 °C. Thus, for example, a compound having a boiling point of 180 °C at normal pressure (~ 100 kPa; 760 torr) would boil at approximately 165 °C at ~ 50 kPa (380 torr), at 150 °C at ~ 25 kPa, etc.